

# Straightforward Immobilization of Phosphonic Acids and Phosphoric Acid Esters on Mesoporous Silica and their Application in an Asymmetric Aldol Reaction

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## Supplementary Material

### Synthesis of SBA-15 silica:

Pluronic P-123 (16.0 g,  $M_n \sim 5800 \text{ g mol}^{-1}$ , Sigma-Aldrich) was dissolved in deionized water (480.0 mL) and hydrochloric acid (48.0 mL, 37 %, Stockmeier). After the addition of TEOS (37.0 mL) the mixture was stirred at 35 °C for 24 h, transferred to a glass-lined autoclave and hydrothermally treated at 80 °C for 24 h. The precipitate was filtered, washed with deionized water and dried at 120 °C prior calcination in a tube furnace at 550 °C for 5 h with a heating ramp of 2.5 °C min<sup>-1</sup> in air.

Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredricksen, G.H.; Chmelka, B.F.; Stucky, G.D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **1998**, *279*, 548-552.

### Synthesis of MCM-41 silica:

Cetyltrimethylammonium bromide (9.6 g, Sigma-Aldrich) was dissolved in deionized water (480.0 mL) and an ammonia solution (41.0 mL, 25 %) and stirred for 5 min. After the addition of TEOS (40.0 mL) the mixture was stirred at room temperature for 24 h, filtered off, washed with deionized water and dried at 120 °C. Calcination was done in a tube furnace at 550 °C for 5 h with a heating ramp of 2.5 °C min<sup>-1</sup> in air.

Kumar, D.; Schumacher, K.; du Fresne von Hohenesche, C.; Grün, M.; Unger, K. K. MCM-41, MCM-48 and Related Mesoporous Adsorbents: Their Synthesis and Characterisation. *Colloids Surf., A* **2001**, *109-116*.

### Synthesis of silica monolith:

Polyethylene glycol (0.616 g, PEG, 35000 g mol<sup>-1</sup>, Sigma-Aldrich) was dissolved in deionized water (6.0 mL) and nitric acid (0.389 g, 30 %, Stockmeier). After the addition of tetraethyl orthosilicate (5.0 mL, TEOS, Sigma-Aldrich) the mixture was stirred until a clear solution was obtained. The H<sub>2</sub>O : HNO<sub>3</sub> : TEOS : PEG molar ratio of the sol was 14.7 : 0.25 : 1.05 : 7.8 · 10<sup>-4</sup>. The solution was transferred to a 96-well microplate, covered and aged for 72 h at 40 °C. Afterwards, the monoliths were transferred to a one molar ammonia solution (Stockmeier) at 90 °C for 24 h, followed by washing with deionized water and drying for 48 h between 40-80 °C. Calcination was carried out in a tube furnace at 550 °C for 5 h with a heating ramp of 0.5 °C min<sup>-1</sup> in air. Before functionalization the monoliths were grinded.

Smått, J.-H.; Schunk, S.; M. Lindén, M. Versatile Double-Templating Synthesis Route to Silica Monoliths Exhibiting a Multimodal Hierarchical Porosity. *Chem. Mater.* **2003**, *15*, 2354-2361.

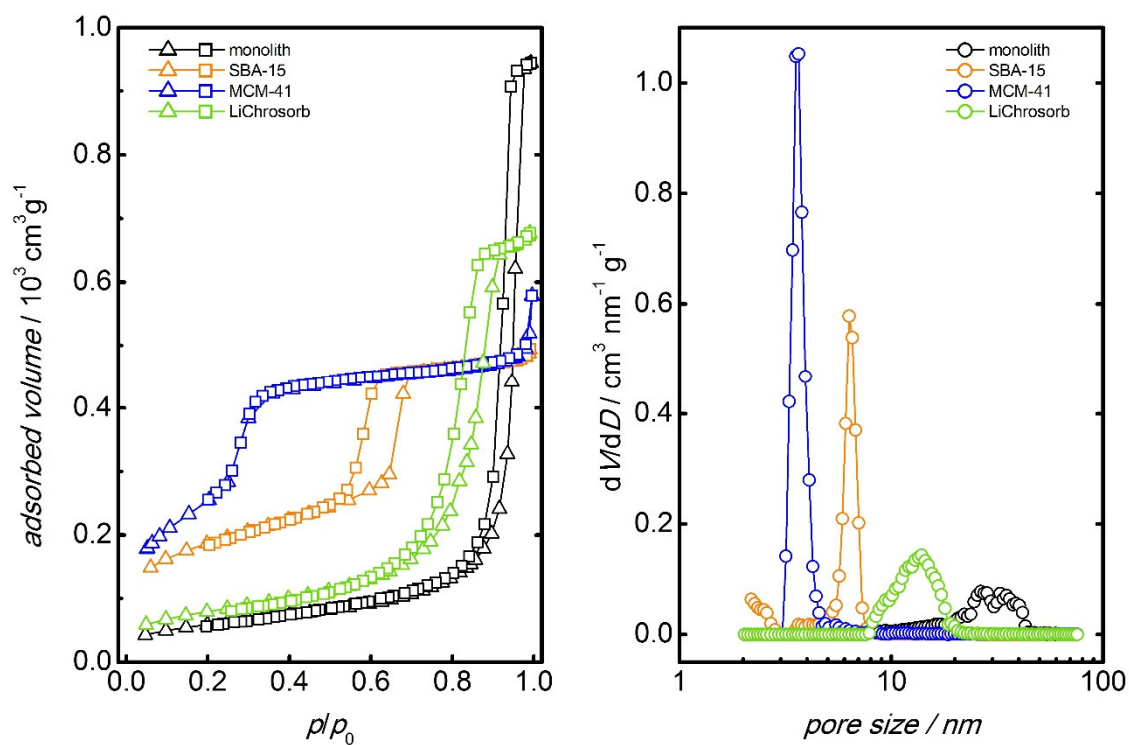


Figure S1.  $\text{N}_2$  physisorption isotherms of the monolith, SBA-15, MCM-41 and LiChrosorb.

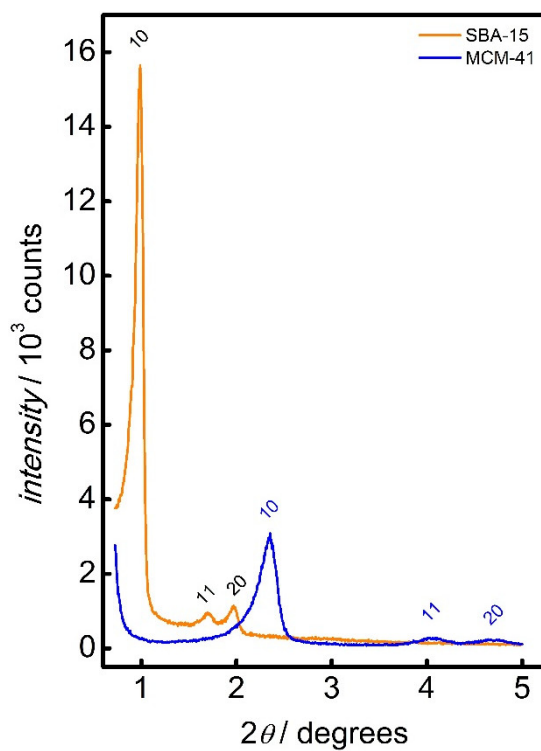


Figure S2. Low angle X-ray diffraction of of SBA-15 and MCM-41.